

Background of the Invention

The present invention relates to carbon technology, and more particularly to highly activated carbons and the use of such carbons in cigarette filters to selectively oxidize or adsorb selected gas phase components.

Certain activated carbons offered commercially show "intrinsic catalytic activity" for oxidation of toxic gaseous molecules such as phosphine, hydrogen sulfide, arsine or sulfur dioxide, to products which form a condensed phase that remains adhering to the carbon. Such carbons include Calgon Carbon Corporation's CENTAUR® carbon (see US 5,356,849, granted October 18, 1994; US 5,444,031, granted August 22, 1995; US 5,464,605, granted November 7, 1995; and US 5,674,462, granted October 7, 1997; all incorporated herein by reference), and NORIT Americas' Vapure 610, 612 or 610P line of carbons. These carbons are both made from coal but by very different processes. CENTAUR® specifically attempts to incorporate nitrogen into the structure by high-temperature treatment with nitrogenous substances such as ammonia or urea. NORIT Vapure has no such explicit nitrogen thermal treatments; however, the intrinsic nitrogen content of the source coal may be sufficient to leave enough in the final product, given an appropriate set of manufacturing conditions. One feature that both carbons have in common that sets them apart from carbons made from coconut shells or wood (for example), is a substantial content of metals (often referred to by the catch-all phrase "ash"). Carbon manufacturers have a significant under-appreciation of the importance of the specific ash components to catalytic activity. Moreover, such producers of activated carbons have a limited understanding of the precise mechanistic details underlying "intrinsic catalytic activity" of carbons so favored with such properties. Of the various metals found

by PIXE analysis to occur in either carbon to extents of hundreds or thousands of parts per million, the one that dominates both is iron. Iron content of either CENTAUR® or NORIT Vapure typically ranges from 0.2 to 0.4% metal by weight.

Summary of the Invention

In accordance with the present invention, catalytically active carbon impregnated with heavy metal is used as a filter element for cigarettes and the selective adsorption and/or oxidation of selected gas phase components in cigarette smoke. The carbons are impregnated with heavy metals and sulfur or nitrogen ligation, and the activity of such carbons is significantly improved by introducing catalytically active sites by heat treatments in the range of 500-1000°C in the presence of heavy metals and nitrogenous materials.

Brief Description of the Drawing

Novel features and advantages of the present invention in addition to those mentioned above will become apparent to persons of ordinary skill in the art from a reading of the following detailed description in conjunction with the accompany drawing wherein similar reference characters identify similar parts and in which:

Figure 1 is a longitudinal cross-sectional view of a cigarette and filter, according to the present invention; and

Figure 2 is a longitudinal cross-sectional view of another cigarette and filter, according to the present invention.

Detailed Description of the Invention

Referring in more particularly to the drawing, Figure 1 shows a cigarette 10 comprising a tobacco rod 12 in combination with a plug-space-plug filter 14. Inner plug 16 and outer plug 18 of filter 14 both comprise cellulose acetate, and space 20 between the plugs is filled with catalytically active carbon 22 impregnated with at least one heavy metal, as explained more fully below. Mainstream tobacco smoke from tobacco rod 12 passes through the catalytically active carbon 22 to selectively adsorb, or selectively oxidize and absorb selected gas phase components in the smoke.

Figure 2 shows a cigarette 30 comprising a tobacco rod 32 with a combined plug filter 34 comprising an inner plug 36 of cellulose acetate and catalytically active carbon 38 impregnated with at least one heavy metal, as explained more fully below. End plug 40 of combined filter 34 may comprise cellulose acetate. Mainstream tobacco smoke from tobacco rod 32 passes through the catalytically active carbon 38 to selectively adsorb or selectively oxidize and adsorb selected gas phase components in the smoke.

Intrinsically active catalytic carbons function as internally short-circuited batteries or fuel cells. Different regions of the carbons (whose internal structure is related to that of graphite) have different oxidation potentials, and can function as electrodes of different potential. Graphitic carbon is electrically conducting, and can provide one of the two "wires" joining the two electrodes. The other "wire" must be provided by an electrolyte, an aqueous phase or film on the surface of the carbon, that, by virtue of a content of ions, can conduct or move protons (H^{\oplus}) electrically, so as to complete the circuit. Such an electrolyte conducts electricity by the net movement of charged ions. As noted below, a movement

of hydrogen cations can be envisioned, since one electrode (the oxygen electrode) consumes hydrogen cation, whereas the other electrode generates hydrogen cation.

- $4H^{\oplus} + 4e^{\ominus} + O_2 \rightarrow 2H_2O$
- $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^{\oplus} + 2e^{\ominus}$
- $H_2S + 4H_2O \rightarrow H_2SO_4 + 8H^{\oplus} + 8e^{\ominus}$
- $PH_3 + 4H_2O \rightarrow H_3PO_4 + 8H^{\oplus} + 8e^{\ominus}$

It is a fundamental property that carbons of the CENTAUR® and Vapure type exert maximal catalytic activity in the presence of water vapor or loaded water content, consistent with the “battery hypothesis.” One of the electrodes may be provided by the bulk carbon, as an “oxygen electrode”, to operate the half-reaction: $4H^{\oplus} + 4e^{\ominus} + O_2 \rightarrow 2 H_2O$. This is a reaction promoted by the presence of acid on the carbon. For the other electrode, the reactions may be:

- $(L)M(+n) \rightarrow (L)M(+n+1) + e^{\ominus}$
- $(L)M(+n+1) \rightarrow (L)M(+n+2) + e^{\ominus}$
- $(L)M(+n) \rightarrow (L)M(+n+2) + 2e^{\ominus}$
- $(L)M(+n+2) + H_2O \rightarrow (L)M(+n) = O + 2H^{\oplus}$
- $(L)M(+n) = O + (\text{substrate}) \rightarrow (\text{substrate} = O) + (L)M(+n)$

The active site functions as an electrode as it is being regenerated to its most oxidized active form. It then sits there as a reagent, awaiting a substrate molecule.

Alternatively, the metal site may bind the targeted substrate (e.g. phosphine or hydrogen sulfide, or even carbon monoxide), and the bound form serves as the electrode to give up electrons towards the oxygen electrode, e.g. in the case of hydrogen sulfide:

- $(L)M(+n) + H_2S \rightarrow (L)M(+n)(H_2S) \quad (\text{binding step})$

- $(L)M(+n)(H_2S) \rightarrow (L)M (+n) = S + 2H^+ + 2e^-$
- $(L)M(+n)=S+H_2O \rightarrow (L)M (+n)=S=O+2H^+ + 2e^-$
- $(L)M(+n)=S=O + H_2O \rightarrow (L)M(+n)=S(=O)_2 + 2H^+ + 2e^-$
- $(L)M(+n)=S(=O)_2 + H_2O \rightarrow (L)M(+n) + S(=O)_3 + 2H^+ + 2e^-.$

In all of the above, M is a metal ion incorporated within the graphitic sheets of the activated carbon so as to be in intimate electronic and electrical contact with the graphitic sheets. L is a ligand to the metal provided by the graphitic sheet. In the equations above, for M(+n), M(+n+1) and M(+n+2), +n(etc) represents the net charge exhibited by the electrode site, rather than the "oxidation state" of metal M since part of the charge resulting from the oxidation state is compensated for by ligand L. Additionally, "n" may be a integer, positive or negative, or zero. Based on a knowledge of chemistry and the constituents of the source coal, L consists of as many as four atoms, of such elements as carbon, nitrogen or sulfur, but most particularly of nitrogen, four of which in an approximately square arrangement can provide a chelating pocket similar to that found in a porphyrin or phthalocyanin. One way to test a porphyrin-like active site is to test its activity in the presence of cyanide or carbon monoxide, in case either of these should deactivate the catalyst. Unlike a simple porphyrin, however, the carbon has enormous reserves of oxidizing power to be called on to oxidize any intruding molecule, due to the electrical conductivity of the whole.

Such pockets of ligated metals in coal-based carbons may have indeed started out as porphyrin molecules in the source coal (coal typically does contain porphyrins derived from the breakdown of primordial chlorophyll). The thermal treatment of coals enroute to activated carbon may well fuse the porphyrin structures into the graphite sheets, forming

a continuous nearly-coplanar array. A small amount of buckling of the graphite sheets would be needed to allow a porphyrin to fit in properly, but the effect would be one of near coplanarity, and excellent electrical conductance between graphite sheet and the included porphyrin-like array.

It may be that Calgon's thermal nitrogen treatments enhance the concentration of porphyrin-like active sites, incorporating the metals intrinsic to the source-coal. In the model above, it is understood that each particle has a multitude of individual "electrodes", and that these are short-circuited amongst each other. Each particle of carbon functions as a multitude of complete battery or fuel cell systems; in the case of a fuel cell, oxygen and a substrate to be oxidized must be provided to the carbon particles.

In accordance with the present invention, catalytically active sites of the "porphyrin" type are introduced in the formation process to carbons that would otherwise have few or no such sites, by heat treatments in the temperature range of 500 to 1000°C of the activated carbon precursors with metal sources and nitrogenous materials together. An optimal means of including such together may involve use of complex cyanides of the metals, i.e. "Prussian blue" (iron hexacyanoferrate) or other hexacyanoferrates (e.g. those of potassium, sodium, ammonium or zinc, etc.) For iron-carbon-nitrogen incorporation, potassium hexacyanocobaltate (for cobalt-nitrogen incorporation), potassium tetracyanonickelate (for nickel-nitrogen incorporation), potassium hexacyanomanganate (for manganese-nitrogen incorporation), potassium hexa- cyanochromate (for chromium-nitrogen incorporation) and the like, as additives for the heat-treatment of the carbonaceous precursors. Alternatively, metal complexes such as iron phthalocyanine, copper (or other metals) phthalocyanines or porphyrins, iron dipyridyl complexes, and iron

orthophenanthroline complexes, or ferrocenes (in conjunction with nitrogenous material) may serve as the simultaneous source of metals and nitrogen. In addition, metals or metal salts or oxides can be simultaneously incorporated into the carbon along with nitrogenous or sulfurous materials. Ferrocene and other sandwich compounds may serve as metal sources in such cases.

Another aspect of the present invention is the simultaneous incorporation of metal and sulfur ligation, as for example, heating coal with iron pyrites (pyrite, iron disulfide) or other metallic sulfides.

This procedure differs from the usual "impregnation" of an activated carbon with metal salts, which typically are effected at low temperature, and which leave the metal on the surface of the carbon, rather than incorporated into the graphitic sheets themselves, so as to provide an internal "electrode". Also, see US 4,578,256, granted March 25, 1986, and incorporated herein by reference.

Still another aspect of the invention is the use of highly activated carbons so made in cigarette filters to selectively oxidize or adsorb selected gas phase components.

The present invention provides catalytically active carbons having much greater throughput or oxidation potential than any currently available from coal. By hugely decreasing the contact times needed to effect oxidative transformations, less carbon is needed for a given application. Also, the precise levels or blends of metals may be rigorously controlled, providing a more uniform activity from batch to batch than currently seen with activated carbon.

Also, by being able to change the surface electron potential of an active carbon, enhanced or decreased affinity for selected classes of compounds with respect to simple adsorption by "ordinary" activated carbons is anticipated to be a benefit of this invention.

For catalytic purposes any of the following heavy metals will help such as Mg, Al, Si, P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, La, Ce, other lanthanides, Hf, Ta, W, Pb and Bi. Excluded from the list of metals are those expected to be reduced to metal during the contemplated heat treatment. Those excluded include Au, Ag and Pt- metals.

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